Table II.

m.	λ.	O−C.
8	3313·5	−0·3
9	3288·9	−0·3
10	3270·4	−0·7
11	3256·6	−0·7
12	3245·9	−0·6
13	3237·8	−0·2
14	3230·6	−0·6
15	3224·6	−0·9
16	3220·3	−0·5
17	3216·4	−0·5
18	3212·9	−0·6
19	3210·1	−0·5
20	3207·7	−0·1
21	3205·6	−0·4
22	3204·0	−0·2
23	3202·4	−0·1
24	3200·7	−0·4

in A of the formula cannot be determined, for the observations used in its calculation have not their possible errors ascribed to them.

Dispersion in Vapours of the Alkali Metals.

By Prof. P. V. Bevan, M.A., Royal Holloway College.

(Communicated by Sir J. J. Thomson, F.R.S. Received January 20,—Read March 9, 1911.)

[Plates 6 and 7.]

In the 'Proceedings' of the Royal Society, A, vol. 84, p. 209, I gave an account of experiments with Potassium vapour, which had for their object the determination of the dispersion curve for the vapour. The effect of the first three pairs of lines of the principal series was quantitatively estimated, and it appeared that certain conclusions could be drawn as to the numbers of systems taking part in the absorption of light. The present communication deals with further experiments of the same kind with vapours of Sodium and Rubidium, and again with the vapour of potassium, as far as regards a temperature effect, which will be discussed later. The experiments were made possible by a grant from the Royal Society, which enabled me to obtain metallic rubidium, and I am glad to take this opportunity of thanking the Government Grant Committee.

In a former paper* I gave results of the measurements of wave-length of the principal series lines for rubidium obtained in the absorption spectrum. This spectrum was obtained by heating rubidium chloride with metallic potassium; enough vapour was formed to give an absorption spectrum showing 25 lines of the series. With metallic rubidium it is easier to get the absorption spectrum, and the list of lines has been extended to include 30 members. A better reading microscope has been available since the original measurements, so that the complete series of lines has been remeasured. The method adopted was the same as that described in the paper referred to, so that there is no need for further description.

The following table gives the measurements of the wave-lengths of the lines of the principal series. The first four members have been measured by Kayser, and the fifth by Ramage. The sixth member appears in some photographs as a pair, but the two lines are close together, and generally broadened somewhat, so that the readings cannot be made so accurately as for later members of the series.

Wave-lengths of Lines of the Principal Series for Rubidium.

1	7950·46	7	3112·95	19	2991·12
	7805·98	8	3082·39	20	2988·94
2	4215·72	9	3060·62	21	2987·01
	4201·98	10	3044·33	22	2985·45
3	3591·74	11	3032·20	23	2984·05
	3587·23	12	3022·72	24	2982·68
4	3351·03	13	3015·16	25	2981·51
	3348·86	14	3009·03	26	2980·52
5	3229·26	15	3004·11	27	2979·62
	3228·18	16	2999·96	28	2978·81
6	3158·25	17	2996·51	29	2978·10
	3157·69	18	2993·52	30	2977·39

With the measuring instrument used, the lines 10–30 should not have any error as great as 0·1 Ångström unit. The measurements were made to 0·01 unit, and are expressed here to that order, but the last figure is not reliable. The lines 8 and 9 could not be determined accurately, but should be within 0·2 of the correct value. In 6 and 7 the accuracy is still less, but there should not be a greater error than 0·3 tenth-metre.

[*Note.*—It is interesting to compare the values of the wave-lengths for the principal series lines of rubidium with the values as given by the formula proposed by Hicks.† For rubidium this formula is

$$n = \mathrm{A} - \frac{\mathrm{N}}{(m+\mu+\alpha/m)^2},$$

---

* 'Roy. Soc. Proc.,' A, vol. 83, p. 421.

† W. M. Hicks, 'Phil. Trans.,' A (190), vol. 210, p. 57.

where N is the universal Rydberg constant 109675, A is 33687·5, μ is 1·366399 for the more refrangible of the pairs of lines and 1·353346 for the less refrangible member, and α is −0·074554 and −0·074382 for the pairs of lines. For lines as high as the sixth of the series account of the difference in the values of α need not be taken. In the observed values the difference between the two members of each pair is not to be detected after the sixth member, and it is therefore a little difficult to decide what exactly to take as the calculated values. The more refrangible component of a pair is the more intense where the members are separable, and therefore the observed value of the centre of the line, where the two appear as one, is probably rather nearer the more refrangible component. In the following list the differences (Observed—Calculated) are given for the one observed and two calculated values after the sixth of the series.

No. of line pair.	O−C.	No. of line pair.	O−C.	No. of line pair.	O−C.
6	−0·19 −0·03	15	−0·11 −0·05	23	+0·05 +0·07
7	−0·31 +0·18	16	−0·11 −0·06	24	−0·06 −0·04
8	−0·17 +0·16	17	−0·08 −0·04	25	−0·09 −0·08
9	−0·11 +0·13	18	−0·14 −0·10	26	−0·08 −0·07
10	−0·29 −0·11	19	−0·01 +0·02	27	−0·07 −0·06
11	−0·18 −0·04	20	−0·02 0·0	28	−0·07 −0·06
12	−0·15 −0·04	21	−0·07 −0·05	29	−0·05 −0·04
13	−0·15 −0·06	22	+0·01 +0·03	30	−0·10 −0·09
14	−0·18 −0·11				

The formula gives very good agreement with the observed values for the pair 6; for 7, 8, and 9 the observed value is between the two calculated values; 10 is not in such good agreement, the observed value being outside the two calculated values, but by very little. The other lines are in good agreement, on the whole, the observed values lying a little to the side of lower wave-length, but in all cases the departure is not more than the estimated possible error. A slight alteration of the constant A such as is possible according to Prof. Hicks' calculations could adjust this. The difference between the wave-lengths of the pairs of lines is considerable up to about the 13th pair in the series, and it ought to be possible to measure the separate members. I hope to be able to do this in the future; measurements of such a character would have considerable interest.]

Fig. 1, Plate 6, is a photograph of a series of the absorption spectra of Rubidium vapour. The vapour was of increasing density for the spectra 1 to 6, after this at decreasing density. The principal series lines are the most evident feature. The continuous absorption for wave-lengths less than the limit of the series is noticeable in 1, 2, 3, especially. This phenomenon is similar to that observed by Wood in the case of sodium. The broadening of the lines is also very evident in the spectra of the denser vapour. Some of the potassium lines appear in these photographs owing to the presence of this metal as impurity.

Rubidium also possesses a channelled-space spectrum, very similar to the spectra of sodium and potassium. This consists of a very large number of lines, with strong absorption at certain intervals, giving the appearance of bands with sharp edges. This spectrum was photographed with a small diffraction grating and laboratory spectrometer, the telescope being replaced by a camera. The aperture and grating being small, detailed examination of the spectrum was impossible, but the wave-lengths corresponding to the heads of the bands were determined. For comparison, the neon red spectrum was used. Three lines were found in this which were not to be discovered in the list of neon lines by Baly. The wave-lengths of these lines are 7032·86, 6929·50, and 6334·61. I have not been able to identify these lines with any belonging to other elements, and assume that they are new lines. The wave-lengths of the edges of the rubidium bands are as follows:—

6734·0
6754·0
6774·9
6796·0
6821·0
6844·2
6871·9
6898·1

The ratios of these numbers to 7950, the wave-length of the line of the first pair of the principal series with greatest wave-length, range from 0·8470 to 0·8676. The corresponding ratios for sodium range from 0·8112 to 0·8706, and for potassium, from 0·8328 to 0·8602.* Carter† has measured the lines of the potassium spectrum, and has given a table with lines marked "very strong" and "strong." These are similar to the lines obtained from Wood's work on sodium, and so may be taken as the edges of the bands. These give numbers for the ratios ranging from 0·8193 to 0·8502. It is an interesting fact that these numbers all fall within the same range. With more light available, more of this type of line would appear for rubidium, and the correspondence be closer still. It is curious that the ratios agree for the more refrangible of the first pair of the principal series—if the less refrangible line be taken, we have no obvious correspondence. Lithium also shows a similar spectrum, situated in the same region, relative to the red lithium line.

---

* 'Phil. Mag.,' January, 1910, p. 199.

† 'Physical Review,' vol. 27, 1908.

There are other points of interest in the rubidium absorption spectrum notably, in the way in which the lines broaden with denser vapour, and in the appearance of lines which seem associated with the principal series lines. These points are, however, still under investigation.

For the dispersion of light due to rubidium vapour, the same method was adopted as was described in the paper already referred to. The vapour prism was in a tube with quartz plates for its ends, and the crossed prism system adopted. The achromatic lens described in the former paper was again used. This lens proves very satisfactory with a small aperture—a larger aperture allows a considerable amount of spherical aberration to spoil the definition. With this lens, an image of a horizontal slit, illuminated by an arc light, is thrown on the slit of the spectrograph. This, without the metallic vapour, gives a linear spectrum. On placing the tube, with metallic vapour in it, in the beam of light, vertical dispersion takes place, and the dispersion curve is seen in the spectrograph. With the quartz spectrograph used there is very little dispersion at the red end of the visible spectrum, but sufficient for photographs to be taken, which showed the complete dispersion curve over a range including all the lines of the principal series except the first pair. The main features of the phenomena to be observed are very similar to those described in the case of the similar experiments with potassium vapour. In the case of rubidium, the pairs of lines are more widely separated than with potassium, so that it is easier to observe the region between the lines of a particular pair. The dispersion effects can be detected on photographs at the first eight members of the series. Measurements could be made at the first four members, which were fairly reliable. At the next two members measurements could be made, but these could only be regarded as giving the order of the effect. As before, the quantities measured were the displacements of the spectrum from its undeviated position at various wave-lengths. These quantities when reduced—to allow for the "tilt" of the plate in the spectrograph—are proportional to the deviation of the rays by the vapour prism, and so are proportional to $n-1$ when n is the refractive index; n being very nearly 1, this is again proportional to n^2-1, and so to the well-known expression of the Sellmeier dispersion formula.

For rubidium, the early lines of the series being pairs separated by a considerable amount, it was found impossible to treat the pair of lines as a single line at a mean position. The case is thus more complicated than that of potassium, as two constants are required for each pair of the series. It appeared that the ratio of these constants for a pair of lines was approximately constant throughout the series. This conclusion is only tentative, as the determination of the ratio of these constants is a matter of considerable difficulty. A very small error in a wave-length used for the determination makes a considerable change in the value of the constant. However, it was assumed that the ratio was the same and this was determined from observations at the second pair of lines. No reliable measurements could be made at the first pair, as the dispersion available was so small. This constant then being determined, its value was assumed for the other pairs, and the values of the separate constants deduced from the observations.

The dispersion formula of Sellmeier for this case can be written

$$n^2-1 = \Sigma\left(\frac{m_1\lambda^2}{\lambda^2-\lambda_1{}^2}+\frac{m_1'\lambda^2}{\lambda^2-\lambda_1'^2}\right),$$

when λ_1, λ_1', are the wave-lengths of the pair of lines, and m_1, m_1', the corresponding constants.

The effect due to the first pair of absorption lines is far larger than that due to succeeding pairs, so that, as was done in the case of potassium, the main part of the dispersion curve—that not in the immediate neighbourhood of the second, third, etc., pairs of lines—was determined first and then detailed observations were made in the regions of the pairs of lines. Several different photographs were used, as those suitable for one region might not be suitable for other parts. The deviations were reduced so as to all be measured on the same scale. With vapour of sufficient density to show the effect at the second and later pairs of lines the red end of the visible spectrum is almost completely absorbed down to a wave-length of about 6400.

The following tables give the measurements of deviations (corrected and reduced to the same scale) for the corresponding wave-lengths.

I.—Deviation for Main Portion.

Wave-length.	Deviation.	Wave-length.	Deviation.
3047	0·6	4500	1·5
3135	0·7	4730	1·9
3190	0·8	5070	2·6
3250	0·9	5500	3·5
3445	0·9	5890	4·9
3969	1·4	6100	5·9
4020	1·5	6350	7·4
4181	2·6		

II.—Deviations near Lines 4202, 4216.

a.		*b.*			
Wave-length.	Deviation.	Wave-length.	Deviation.	Wave-length.	Deviation.
4132 ·5	−1 ·65	3933 ·8	−1 ·5	4214 ·5	−2 ·7
43 ·7	−1 ·75	68 ·6	−1 ·5	15 ·0	−3 ·0
54 ·5	−1 ·84	4158 ·0	−2 ·0	15 ·5	−4 ·0
72 ·2	−2 ·05	68 ·0	−2 ·2	17 ·5	+2 ·7
77 ·7	−2 ·2	81 ·0	−2 ·5	19 ·0	2 ·0
81 ·8	−2 ·47	86 ·0	−2 ·7	20 ·0	1 ·7
87 ·5	−2 ·75	90 ·0	−3 ·0	20 ·5	1 ·3
91 ·6	−3 ·2	92 ·5	−3 ·3	21 ·5	1 ·0
95 ·5	−4 ·3	96 ·5	−4 ·0	22 ·0	0 ·7
98 ·4	−6 ·2	98 ·5	−5 ·0	23 ·0	0 ·3
99 ·2	−7 ·3	4200 ·5	−6 ·7	24 ·0	0 ·0
4210 ·5	+0 ·6	1 ·5	−8 ·3	30 ·0	−0 ·7
19 ·5	−0 ·6	6 ·0	+2 ·3	37 ·0	−1 ·0
22 ·6	0 ·0	7 ·5	1 ·7	50 ·0	−1 ·2
27 ·6	+0 ·5	8 ·5	1 ·0	75 ·0	−1 ·3
50 ·6	1 ·15	9 ·0	0 ·7	4308 ·0	−1 ·5
60 ·6	1 ·15	10 ·0	0 ·3	25 ·0	−1 ·5
71 ·6	1 ·2	11 ·0	0 ·0	84 ·0	−1 ·7
82 ·6	1 ·15	11 ·5	−0 ·3	4405 ·0	−1 ·7
94 ·3	1 ·3	12 ·0	−0 ·7		
99 ·4	1 ·3	12 ·5	−1 ·0		
4308 ·0	1 ·4	12 ·8	−1 ·3		
25 ·9	1 ·6	13 ·0	−1 ·7		
83 ·7	1 ·6	13 ·5	−2 ·0		
4404 ·9	1 ·6	14 ·0	−2 ·3		

In Table II, *a*, the wave-lengths are of iron lines. The first horizontal slit was illuminated by an iron arc and so the deviated spectrum consisted of points corresponding to the iron lines. In this way the wave-lengths were accurately known, but the spots on the negative were somewhat blurred and the deviation measurements were not so reliable as in *b*, which consists of measurements made on a photograph taken with the ordinary carbon arc. The deviations have been reduced so that all are on the same scale as that of Table I.

III.—Deviations near Lines 3587, 3592.

Wave-length.	Deviation.	Wave-length.	Deviation.
3538	−1 ·0	3590 ·47	−1 ·0
3556	−1 ·2	3591 ·28	−1 ·3
3580 ·9	−1 ·4	3591 ·74	
3583 ·4	−1 ·8	3592 ·36	+0 ·6
3584 ·8	−2 ·2	3592 ·55	+0 ·2
3585 ·6	−2 ·5	3592 ·90	−0 ·2
3586 ·1	−2 ·9	3593 ·44	−0 ·4
3586 ·4	−4 ·2	3594 ·65	−0 ·6
3587 ·2		3595 ·86	−0 ·8
3589 ·0	+0 ·6	3600 ·7	−1 ·0
3589 ·3	−0 ·2	3622 ·9	−1 ·0
3590 ·06	−0 ·6		

IV.—Deviations near Lines 3349, 3351.

Wave-length.	Deviation.	Wave-length.	Deviation.
3339·5	−0·9	3351·3	−0·1
3344·8	−1·0	3351·7	−0·3
3347·1	−1·1	3352·3	−0·5
3347·6	−1·3	3355·8	−0·7
3348·2	−1·7	3365·0	−0·8
3350·0	−0·5		

V.—Deviations near Lines 3228, 3229.

Wave-length.	Deviation.	Wave-length.	Deviation.
3225·1	−0·8	3228·7	
3226·8	−1·0	3229·4	−0·6
3227·2	−1·4	3232·6	−0·7
3227·4	−1·6	3238·1	−0·8

VI.—Deviations near Line 3158.

Wave-length.	Deviation.	Wave-length.	Deviation.
3155·4	−0·8	3158·6	−0·4
3157·1	−1·0	3159·6	−0·6
3157·6	−1·3	3163·1	−0·8

By plotting the main curve and deducting the values of deviation corresponding to the first pair of lines from the observations near succeeding pairs, we obtain the deviation at various wave-lengths as far as they depend on any particular pair of the series, for the influence of any pair after the first is confined to the immediate neighbourhood of the lines. In this way we obtain the observed deviations, which are proportional to the quantity

$$\frac{m_2\lambda^2}{\lambda^2-\lambda_2^2}+\frac{m_2'\lambda^2}{\lambda^2-\lambda_2'^2},$$

and the corresponding quantities for higher members of the series.

From these quantities we can find the values of the constants m_2, m_2', etc. With the large number of observations made it was a little difficult to decide how to obtain the best values of the constants. The method of least squares would have been laborious, and, as the observations are of very varying weights, it was thought that no great advantage would be obtained by applying it. Near the absorption lines slight errors in wave-length determination would involve large errors in the calculated constants, and where these errors would be small, at some distance from the absorption lines, the small deviations become uncertain in measurement. It is difficult to balance these two sources of error, so the method adopted was to plot all the observations and find values of the constants which gave a curve fitting the observations as well as possible. The two constants m and m', as has already been remarked, seemed to have about the same ratio for each pair of lines, so that this ratio was determined once for all from the observations in Table II for the second pair of lines and was assumed to be the same for the other pairs.

The values of the constants obtained are as follows:—

Constants.	Corresponding wave-lengths.	Constants.	Corresponding wave-lengths.
1 m_1 = 2·71 m_1' = 0·90	7805·98 7950·46	4 m_4 = $3{\cdot}0 \times 10^{-4}$ m_4' = $1{\cdot}0 \times 10^{-4}$	3348·86 3351·03
2 m_2 = $7{\cdot}5 \times 10^{-3}$ m_2' = $2{\cdot}5 \times 10^{-3}$	4201·98 4215·72	5 m_5 = $2{\cdot}5 \times 10^{-4}$ m_5' = $0{\cdot}8 \times 10^{-4}$	3228·18 3229·26
3 m_3 = $10{\cdot}0 \times 10^{-4}$ m_3' = $3{\cdot}3 \times 10^{-4}$	3587·23 3591·74	6 m_6 = $1{\cdot}5 \times 10^{-4}$ m_6' = $0{\cdot}5 \times 10^{-4}$	3158·2 3157·7

The values for 5 and 6 are very doubtful, as the deviations are so small except very close to the absorption lines. For example, the observations for m_6' gave three values, 0·7, 0·5, and 0·2, multiplied by 10^{-4}. These values, therefore, can only be regarded as giving an estimate of the order of the effect.

In text-fig. 1 the dispersion curve is plotted for the range from 6300 to 3200. The region of longer wave-length is not shown, as the curve would not show the effects at the second, third, and fourth lines if on a small enough scale to show the curve at the red lines. Also, with the apparatus at my disposal, sufficient accuracy could not be obtained in the determination of wave-lengths in the red region owing to the small dispersion available. The curve represents the quantity

$$\sum_1^4 \left(\frac{m_1\lambda^2}{\lambda^2-\lambda_1^2} + \frac{m_1'\lambda^2}{\lambda^2-\lambda_1'^2} \right),$$

with the values of the constants above. The observed values of deviations are indicated by points which lie very fairly closely about the curve.

In fig. 2 (p. 68) the ordinates represent the quantity

$$\frac{m_1\lambda^2}{\lambda^2-\lambda_1^2} + \frac{m_1'\lambda^2}{\lambda^2-\lambda_1'^2} + \frac{m_2\lambda^2}{\lambda^2-\lambda_2^2} + \frac{m_2'\lambda^2}{\lambda^2-\lambda_2'^2},$$

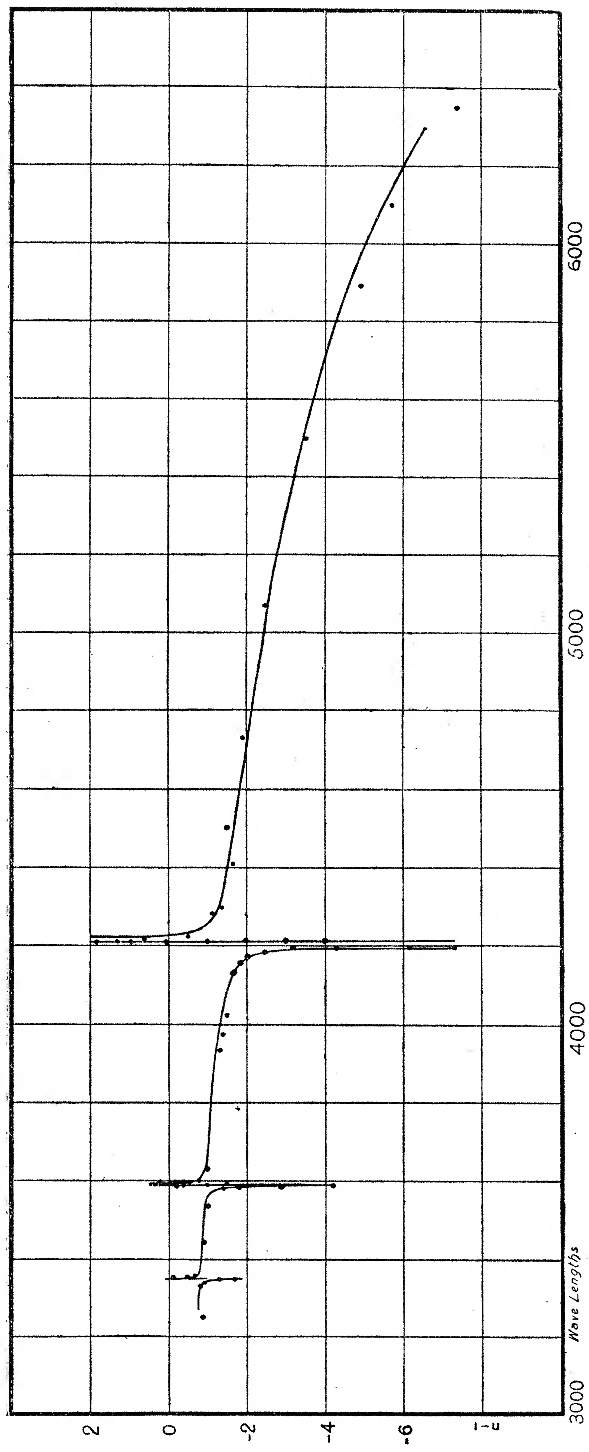

FIG. 1.—Dispersion Curve for Rubidium vapour:—

$$n-1 = \frac{0\cdot90\lambda^2}{\lambda^2-7950^2} + \frac{2\cdot71\lambda^2}{\lambda^2-7806^2} + \frac{2\cdot5\times10^{-3}\lambda^2}{\lambda^2-4215^2} + \frac{7\cdot5\times10^{-3}\lambda^2}{\lambda^2-4202^2} + \frac{3\cdot3\times10^{-4}\lambda^2}{\lambda^2-3592^2} + \frac{10\cdot0\times10^{-4}\lambda^2}{\lambda^2-3587^2} + \frac{10^{-4}\lambda^2}{\lambda^2-3351^2} + \frac{3\cdot0\times10^{-4}\lambda^2}{\lambda^2-3349^2}.$$

The points marked are observed values.

the second two terms of which we can regard as the deviation due to the second pair of the lines of the principal series. The scale is much larger than that of fig. 1. The observed deviations are represented by points and crosses. The points refer to the observations *a* of Table II, the crosses to those of *b* in the same table. The observations *a* were from a photograph with the iron arc as source of light, so that the wave-lengths are accurately known; the deviations are, however, not so good as for the observations *b*.

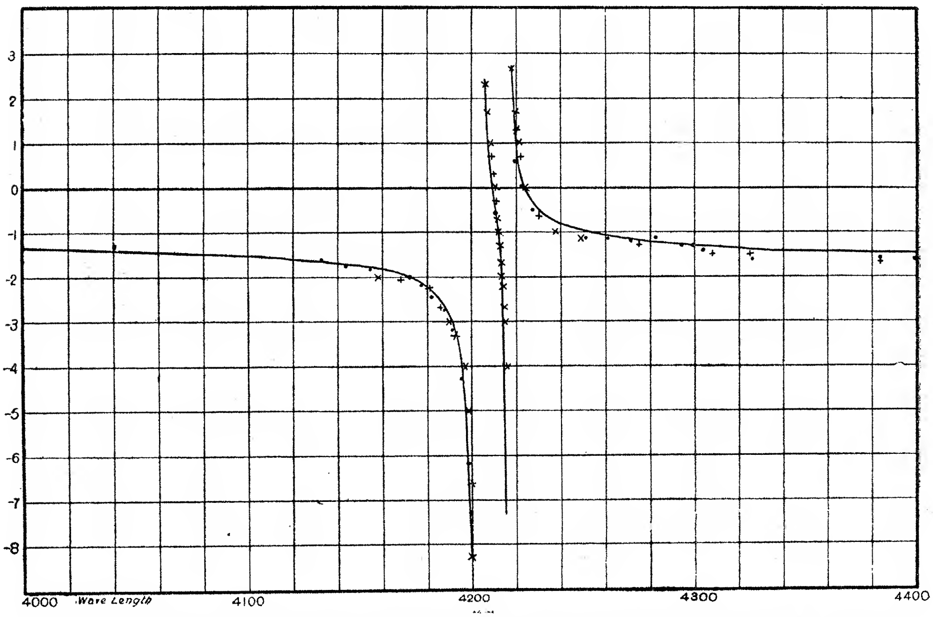

Fig. 2.—Dispersion Curve in the neighbourhood of lines 4216, 4202. Rubidium vapour.

Figs. 3 and 4 (p. 69) represent the quantities

$$\frac{m_3\lambda^2}{\lambda^2-\lambda_3^2}+\frac{m_3'\lambda^2}{\lambda^2-\lambda_3'^2} \quad \text{and} \quad \frac{m_4\lambda^2}{\lambda^2-\lambda_4^2}+\frac{m_4'\lambda^2}{\lambda^2-\lambda_4'^2},$$

so that the ordinates may be taken to represent the deviations due to the third and fourth pairs of the principal series of lines. The points represent the observations recorded in Tables III and IV.

In this series of curves the points representing observed deviations are found to lie very fairly closely about the curves. Better agreement could perhaps be found if a more elaborate method of determining the constants were employed, but there seemed no reason at present for the enormously increased arithmetic necessary for an application of the method of least squares to the observations.

Fig. 2 of Plate 6 is a photograph of the dispersion effect in the neighbourhood of the red lines; *b* is the photograph as taken, and *a* is an enlargement without retouching. The curve as seen in the spectroscope is very beautiful, showing the region between the two lines very clearly. This photograph was taken with a simple spectroscope with one flint glass prism, so that there is very little dispersion between the lines 7950 and 7806. Fig. 3 is interesting as showing a dispersion curve for three absorption lines; the vapour for this photograph was a mixture of potassium and rubidium. Rubidium chloride was heated in a tube with potassium, and a considerable quantity of rubidium vapour set free. The dispersion was small, so that the

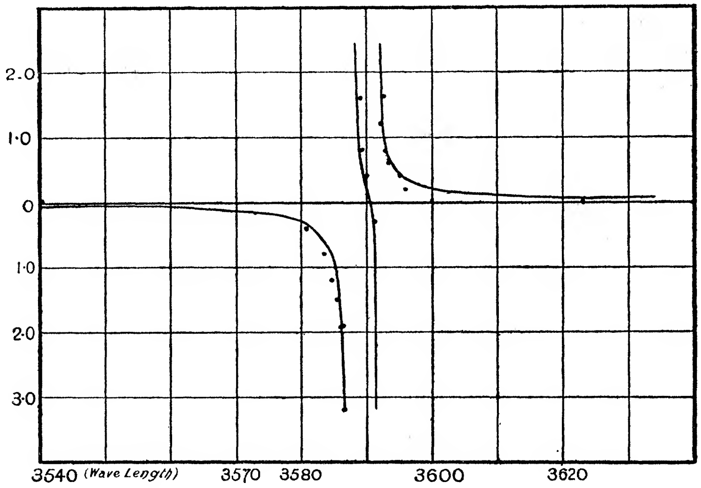

Fig. 3.—Dispersion near 3592, 3587, in Rubidium vapour.

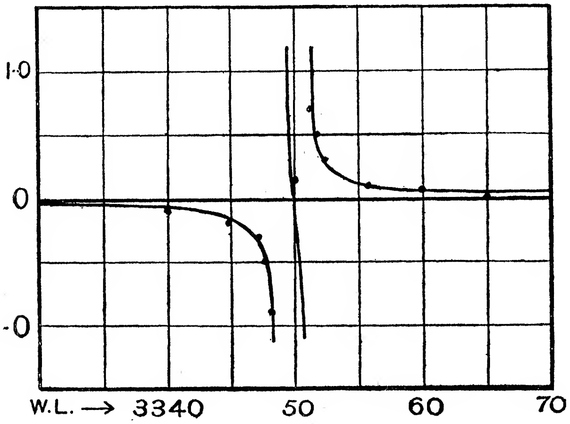

Fig. 4.—Dispersion near 3351; 3349.

two potassium lines 7699 and 7665 have effect as only one line. In fig. 2, just to the left of 7806, the slight effect of potassium as impurity in the rubidium is visible.

In Plate 7, fig. 4, two photographs of the effect at the rubidium lines 4215, 4202, are shown; *a* and *b* are enlargements of *c*; *a* is with denser vapour than *b*. To the left of the photographs the effect at the next pair of lines also appears—3591, 3587. In these photographs the potassium impurity also shows itself by the slight break at the lines 4047, 4044. Fig. 5 shows the effect at the third and succeeding pairs of lines; *a* is again an enlargement of *b*. The position of the undeviated spectrum was also photographed on this plate. This photograph shows also a good number of the absorption lines nearer the limit of the series. The potassium line at 3447 also appears. Fig. 6 gives examples of the dispersion curves photographed with the undeviated spectrum at the lines 4215, 4202, and the pair at 3590.

Sodium.

For the case of sodium the dispersion corresponding to the D lines has been investigated by Wood.* He, however, has not made measurements of the dispersion corresponding to the other lines of the principal series, and it seemed worth while to obtain values of the constants for sodium to see if there might be a general relation to be found in the values of these constants for the alkali metals. Wood has investigated the dispersion between and near to the D lines, but his numbers do not enable us to obtain any reliable value of the ratio of the two separate constants for the D lines. All that can be said is that the constant for the line of smaller wave-length is greater than the other, in accordance with the observed results for rubidium and potassium, and with the fact that the line of shorter wave-length of all the pairs of these series for the alkali metals is more intense than the other.

Sodium is, for dispersion near lines other than the D lines, more difficult for investigation than the other metals of the group except lithium. This is owing to the fact that a higher temperature is necessary to obtain the vapour in sufficient density. With sodium, however, the first pair of the principal series is in a more suitable part of the spectrum for visual observation and also for photographic methods, the red end, where the potassium, rubidium, and cæsium lines occur, being more difficult to see and photograph than the yellow. The dispersion effects could only be measured with any accuracy at the lines 3304 and 2853. The effect could be observed at the two next pairs of lines, but no reliable measurements could be made. For the sodium measurements, instead of a slit as source of light, the naked arc was used, with a grating of fine wires wound on a wooden frame in front of this. The plane of the wires being nearly horizontal, they were at different distances from the lens used to focus them on the slit of the spectroscope, so that with a rough adjustment of focus some of the images of the wires would be in good focus on the spectroscope slit after the heated tube was introduced. This device saved a good deal of trouble in focussing.

---

* 'Phil. Mag.,' [6], 1904, vol. 8, p. 293.

The following table gives the results for deviations and wave-lengths:—

Wave-length.	Deviation.	Wave-length.	Deviation.	Wave-length.	Deviation.
5760	134	3372	0·6	2900	0
5620	59	3322	1·9	2865	0·2
5550	47	3317·4	2·4	2857·7	0·7
5410	31	3313·4	4·4	2856·7	1·1
5300	20	3312·2	5·4	2855·3	2·5
4500	9·2	3309·3	6·4	2854·3	3·7
4450	6·5	3295·9	−5·1	2851·8	−3·0
4220	6·4	3294·3	−4·1	2850·9	−1·7
3970	4·9	3292·3	−3·1	2849·5	−0·8
		3288·7	−2·6	2845·5	−0·3
		3274	−1·6	2800	0
		3200	−0·3		

The deviations in the second two columns are from the mean position of the curve, not the whole deviations; they represent, therefore, the quantities

$$\frac{m_2\lambda^2}{\lambda^2-\lambda_2{}^2}, \quad \frac{m_3\lambda^2}{\lambda^2-\lambda_3{}^2},$$

λ_2, λ_3, being the mean wave-lengths of the second and third pair of lines for the sodium series.

The deviations in the first column give the data for the main part of the dispersion curve,

$$n^2-1 = \frac{m_1\lambda^2}{\lambda^2-\lambda_1{}^2}, \ \lambda_1 \text{ being } 5890.$$

Using the measured deviations instead of n^2-1 we obtain for m_1 for this set of observations 5·85. From the other deviations we obtain $m_2 = 2{\cdot}30 \times 10^{-2}$ and $2{\cdot}92 \times 10^{-3}$. In fig. 5, I, the curve is traced with these values of the constants, and the observed values of deviations marked by crosses. These points, near the lines 3303, 2853, were obtained by adding the observed deviations of the above table to the calculated value, taking only the first term of the Sellmeier formula. In other words, the observed deviations are only observed partly—their values measured from the position corresponding to the deviation produced by the first line. In Curve II, fig. 5, the part of the curve nearer the D lines is drawn. The scale for this curve is much smaller than for I, and is shown on the right-hand side of the diagram. It will be noticed that the point representing deviation at 5300 does not lie on the curve, and its departure is greater than was to be expected. The deviation at 4500 is also off the curve in the opposite sense, though here it is possible the departure from the curve might be explained as a bad measurement. These two positions are just at the ends of the channelled space absorption spectrum, investigated by Wood, and for the present case this region was almost completely dark, practically all the light being absorbed. We should expect a band of this sort to involve changes in the dispersion, and these observations seem to indicate this—the departures of the points from the normal deviation are in the right direction. I have observed a similar phenomenon in the case of potassium near the corresponding absorption region, but the point wants further investigation.

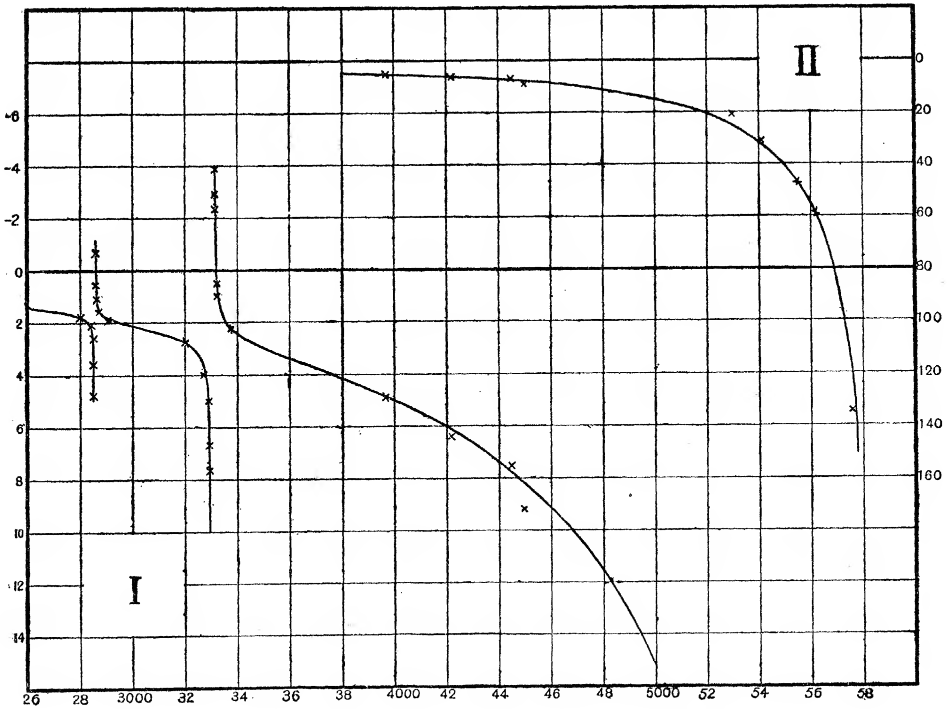

Fig. 5.—Dispersion curves for sodium vapour.

The Question of the Effect of Temperature on the Relative Values of the Constants of the Dispersion Formula.

If attention be confined to the effects of dispersion near any single pair of lines, the constant of the dispersion formula appropriate to this line increases with the temperature of the vapour used. It is not quite clear whether it is the density gradient or the prismatic form of the vapour in the tube which produces the dispersion effect, or whether both of these causes co-operate. I am inclined to think that the second effect is of most importance, but in any case, if the tube is heated more strongly, we get a vapour of greater average density and so greater dispersion effects. The question naturally occurs as to whether the different constants change proportionally with this change of average temperature in the vapour. On the view that was put forward in my earlier paper,* to which reference has already been made, that different specialised atoms are engaged in the absorption of the different lines, it seems probable that the relative numbers of these special atoms should depend on the temperature of the vapour. If more complex systems are required for the absorption corresponding to higher members of the series of lines, it seems likely that the relative number of atoms corresponding to the higher members should decrease with increase of temperature. We should expect, therefore, a change in the relative values of the constants m_1, m_2, etc., which would appear as an increase in the ratios m_1/m_2, m_2/m_3, etc., with increase in temperature. An effect of this kind was therefore sought in the case of potassium and sodium. As will appear, there is evidence for an increase in these ratios which is fairly conclusive. The actual determination of the constants has, of course, a considerable amount of uncertainty, but a large number of measurements were made, and there does seem to be a definite increase in the ratios indicated. For the case of sodium three photographs were used with different densities of vapour. For the most dense vapour the absorption was complete in the region 5000 to 4600. This photograph was the one used for the measurements for the sodium dispersion curve already described. The next of the series of three gave dispersion in the region near the D lines of rather less than one-half that occurring in the first. On this photograph measurements could be made giving fairly good values of the constants corresponding to the first three lines of the series. The third photograph was with vapour of considerably less density, and the effect at the third line was too small for any reliable measurements. Measurements of deviations were made at a number of points near the absorption lines, so that several of the values of the constants could be obtained.

---

* 'Roy. Soc. Proc.,' A, vol. 84, p. 209.

The following tables give the observed values of the constants; all observations are taken into account, excepting in cases where the measurement was clearly bad, owing either to the deviated spectrum being indistinct, or the wave-length at the particular position differing so little from that of the absorption line that the effect of the possible error in its determination was too large :—

Sodium (1).

m_1	6·00	5·94		Mean, 5·85
	5·96	5·67		
	5·75	5·89		
	5·92	5·77		
	5·83			
	5·81			
$m_2 \times 10^2$......	2·44	2·15	2·18	Mean, 2·30
	2·31	2·04	2·10	
	2·49	2·17	2·16	
	2·64	2·32	2·12	
	2·76	2·20	2·46	
	2·27	2·10		
$m_3 \times 10^3$......	2·35	2·75	3·12	Mean, 2·92
	2·47	3·24	3·46	
	2·53	3·18	3·33	
	2·89	2·50		
	2·90	3·19		

Sodium (2).

m_1	2·36	2·18	2·25	Mean, 2·24
	2·26	2·35	2·36	
	2·34	2·19	2·27	
	2·02	2·32		
	1·99	2·50		
$m_2 \times 10^2$ ...	1·09	1·09	0·98	Mean, 1·02
	1·01	1·00	1·11	
	1·00	0·98	0·96	
	1·02	1·01	0·92	
	1·02	1·01	1·08	
	1·02	1·08	0·97	
	1·10	0·99		
	1·09	0·96		
$m_3 \times 10^3$......	1·36	1·27		Mean, 1·33
	1·42	1·35		
	1·23	1·36		

Sodium (3).

m_1	0·493	0·516	Mean, 0·499
	0·479	0·500	
	0·520	0·515	
	0·472	0·498	
$m_2 \times 10^3$......	2·15	1·98	Mean, 2·36
	2·54	2·50	
	2·60	2·68	
	2·04	1·92	
	2·46	2·44	
	2·50	2·50	

We obtain from the mean values of these constants the following table:—

	(1).	(2).	(3).
m_1/m_2 ………	254	220	211
m_2/m_3 ………	7·9	7·7	

The difference between the ratio m_1/m_2 in the two cases (1) and (2) is considerable, and although the individual values of the constants differ in any particular case by considerable amounts, yet the indication of a decrease in the ratios is fairly strong.

In the case of potassium the evidence is rather stronger. A series of three photographs was taken with potassium with decreasing density of vapour. Clearer definition was obtained in the potassium photographs; the device of the wire grating was used for these. An example of the type of photograph is represented in fig. 7, Plate 7.

The following are the results:—

Potassium (1).

m_1 ………………	38·2		
	36·0		
	35·0		Mean, 36·4
	36·5		
	36·4		
$m_2 \times 10^2$ …………	5·93	6·35	
	5·62	6·18	
	6·00	6·60	Mean, 6·21
	6·25	6·50	
	6·25	6·48	
$m_3 \times 10^3$ …………	5·45	5·37	
	5·35	5·52	
	5·15	5·42	Mean, 5·45
	5·50	5·75	
	5·51		

Potassium (2).

m_1 ………………	4·65	4·76	
	4·63	4·70	Mean, 4·63
	4·65	4·75	
	4·40	4·54	
$m_2 \times 10^3$ …………	9·17	8·65	
	9·09	9·25	Mean, 9·15
	9·55		
	9·20		
$m_3 \times 10^3$ …………	1·32		
	1·14		Mean, 1·36
	1·40		
	1·56		

Potassium (3).

m_1	2·36	2·47	Mean, 2·42
	2·26	2·53	
	2·32	2·52	
	2·44		
$m_2 \times 10^3$	6·59	6·64	Mean, 6·43
	6·51	6·24	
	6·29	6·29	
$m_3 \times 10^4$	7·2	9·3	Mean, 9·2
	8·7	10·5	
	9·8	9·6	

These numbers give us the following table for the ratios m_1/m_2, m_2/m_3:—

	(1).	(2).	(3).
m_1/m_2	587	507	376
m_2/m_3	11·2	6·7	7·0

The values of the constants in (1) are the best; in this case the measurements of deviation were largest, and so admit of fair accuracy. For the measurements (2) the accuracy is fairly good for m_1 and m_2; m_3 is, however, uncertain, wide differences occurring in the four values obtained. For (3) m_1 and m_2 are fairly good values, but m_3 again shows wide variations in the individual numbers. Still, allowing for the uncertainty in the observations, the diminution in the numbers for m_1/m_2 and the greater value of m_2/m_3 for (1) indicates pretty clearly that there is a real change in the relative values of the constants. The values 6·7 and 7 for m_2/m_3 from (2) and (3) are so near together, and the individual differences in the values of m_3 for (2) and (3) are so great, that the apparent increase from 6·7 to 7 is of no significance.

These numbers for potassium with those of a similar character for sodium seem to indicate a real change dependent on the temperature of the vapour.

This being so, we cannot expect any relation between the constants of the different metals, as before any such relation should appear we must have the vapours of the metals at corresponding temperatures, and as yet there is no evidence to show at what temperatures we should expect correspondence to exist.

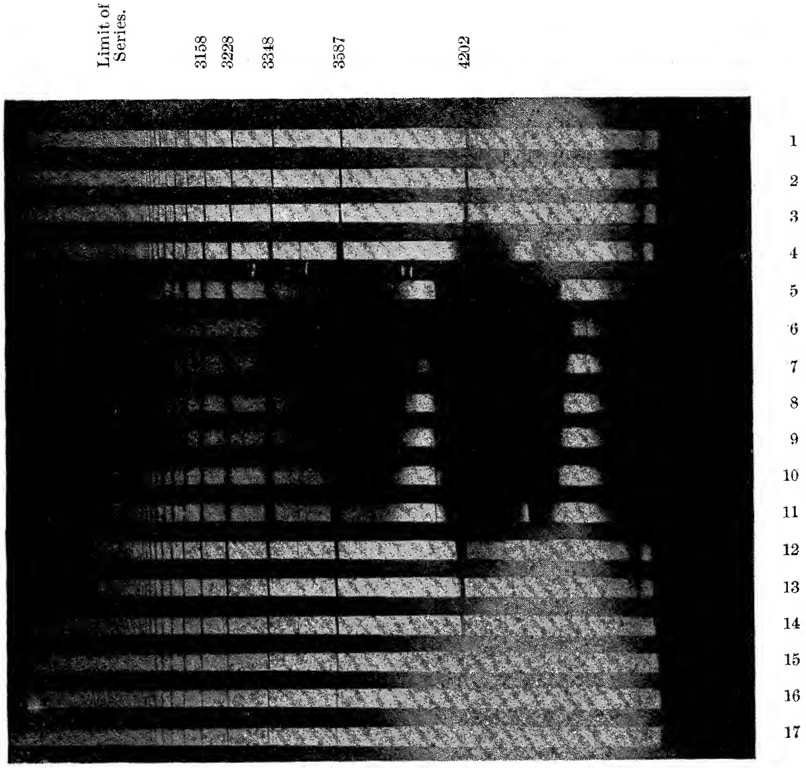

FIG. 1.

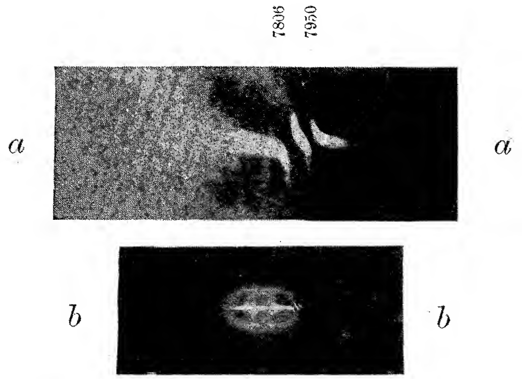

FIG. 2.

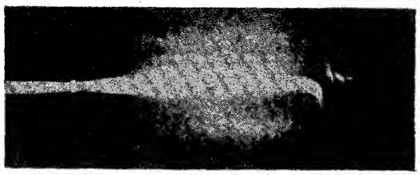

FIG. 3.

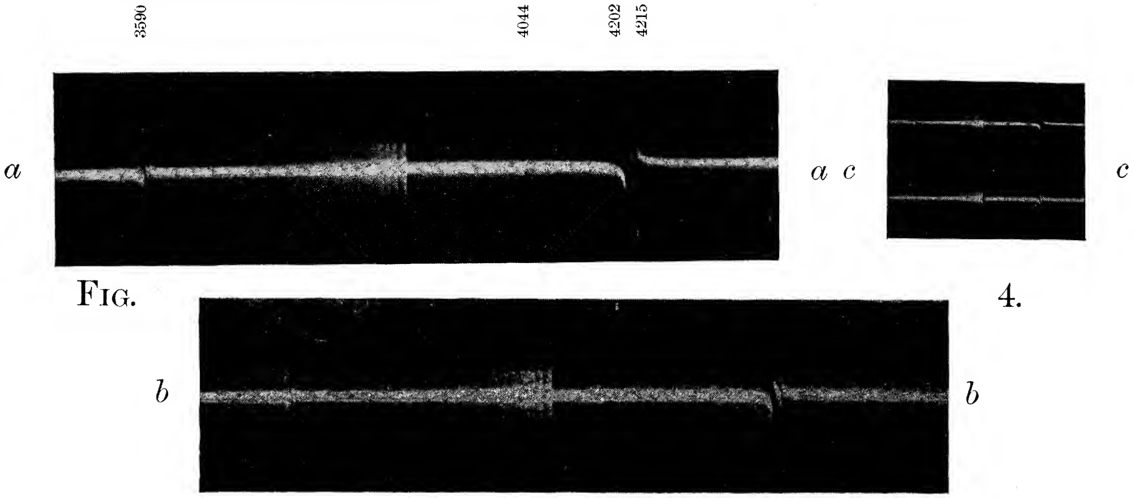

FIG. 4.

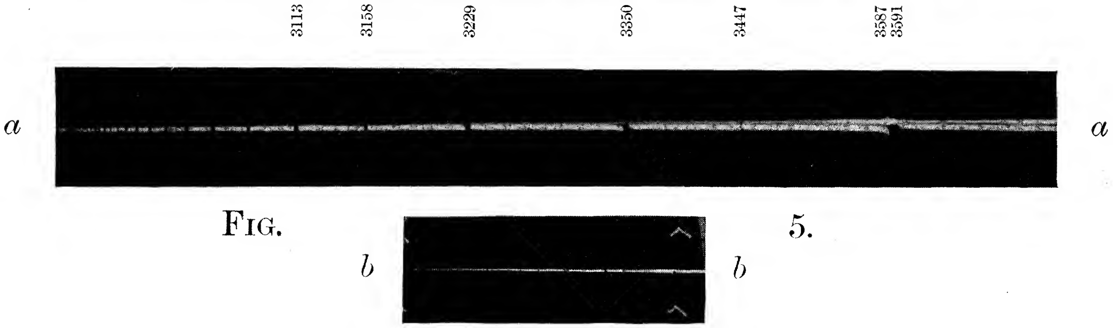

FIG. 5.

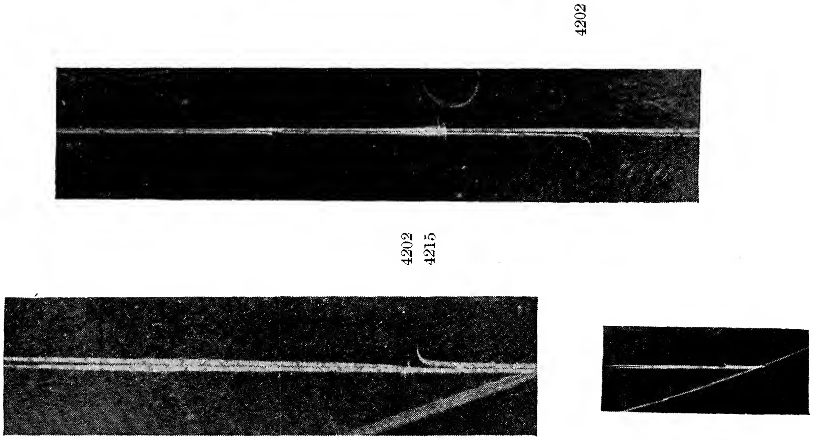

FIG. 6.

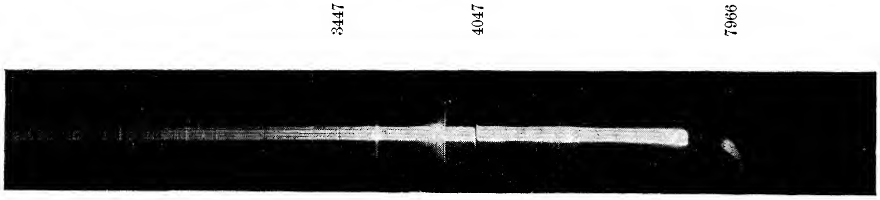

FIG. 7.

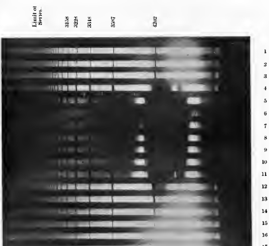

FIG. 1.

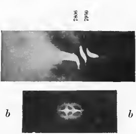

FIG. 2.

FIG. 3.

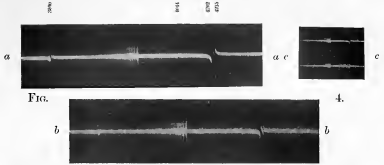

FIG. 4.

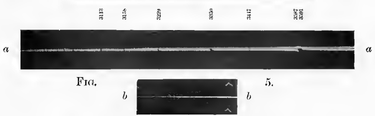

FIG. 5.

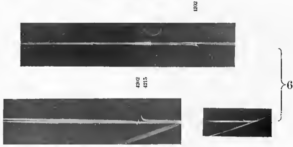

FIG. 6.

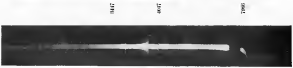

FIG. 7.